Journal of Chromatography, 555 (1991) 291–296
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 398

Short Communication

N-(Hydroxymethyl)thioamide resin as stationary phase in ion-exchange chromatography for metal ion separation

C. Y. LIU*, M. J. CHEN and T. J. CHAI
Department of Chemistry, National Taiwan University, Taipei (Taiwan)

(Received April 24th, 1991)

ABSTRACT

The sorption properties of Ag(I), Au(III), Cd(II), Co(II), Cu(II), Fe(III), Hg(II), Ni(II), Pb(II), Pt(IV) and Zn(II) on N-(hydroxymethyl)thioamide resin using perchloric acid and hydrochloric acid at various concentrations were studied. The effect of foreign ligands on the retention of metal ions was also investigated. The chromatographic properties of this resin as a stationary phase in ion-exchange chromatography for the separation of cobalt, copper, gold, iron, mercury, platinum, silver and zinc are described. Separations were achieved in many instances by using a mineral acid containing chloride or sulphate anions. Quantitative chromatographic analysis was possible for a variety of sample types. The suitability of the resin for metal preconcentration for both single elements and metal ion mixtures is also described.

INTRODUCTION

To determine metal ions at low levels in complex matrices, three different methods using high-performance liquid chromatography (HPLC) can be applied. The ion chromatographic method is the most common, but often requires the use of a metal complexing additive in the buffered eluent [1]. Reversed-phase HPLC is also popular, but the sample mixture to be separated must be converted into neutral metal chelates [2–7]. Another method is a hybrid of the above two methods, and a more direct approach. Pretreatment of the sample solution is generally not necessary, and a simple mobile phase can be used because selectivity is designed into the stationary phase. A chelating resin used as stationary phase is an example [8].

In ion chromatography, originally the suppressed approach was mainly used, but published results with the non-suppressed column technique subsequently encouraged its application, as conventional LC equipment can be used. Columns other than the normal ion-exchange type can also be used for the technique of ion chromatography [1]. A reliable method for the preparation of a chelating resin containing sulphur and oxygen donors from an acrylonitrile–divinylbenzene co-

0021-9673/91/$03.50

polymer and studies of the chelating behaviour of the resin have previously been reported [9]. The chelate-forming properties of this resin appeared to be promising, and the work has now been extended to apply it as the stationary phase in ion-exchange chromatography in the separation of some metal ions.

EXPERIMENTAL

Apparatus

A Dionex Model 2000i ion chromatograph and a Dionex UV–VIS detector were used. A sample loop of 50 μl was employed, and a Chem Inert glass column (50 mm × 6 mm I.D.) packed with 100–200-mesh N-(hydroxymethyl)thioamide resin was used for separations.

Preparation of resin

The N-(hydroxymethyl)thioamide resin was synthesized in our laboratory. Detailed procedures for the preparation and some of the properties of this resin have been described in a previous paper [9].

Determination of sorption properties in strongly acidic solution

Air-dried resin samples (0.03 g) were equilibrated by mechanical shaking with 25 ml of 4×10^{-4} mol l^{-1} solutions of the individual metal salts in a strongly acidic medium, using either perchloric acid or hydrochloric acid. After a shaking time of 24 h at 25 ± 0.02°C, aliquots were taken from the aqueous solutions and analysed spectrophotometrically. The distribution coefficients D were calculated in the usual way.

General chromatographic conditions

Chromatograms were generally run at ambient temperature of a flow-rate of 1 ml min^{-1}. All mobile phases were degassed ultrasonically before use. Prior to sample injection, the column was equilibrated with the eluent for at least 0.5 h at 1 ml min^{-1}. The columns were considered to be equilibrated when the acidity of the effluent matched that of the entering mobile phase to within ±0.02 pH unit, when a stable baseline was obtained and when two successive injections of sample yielded the same retention time.

The 4-(2-pyridylazo)resorcinol (PAR) flow-rate was generally half that of the mobile phase, the latter being 1.0 ml min^{-1}. The detector was set at 520 nm or direct UV detection of the chloride complexes at 215 nm was applied.

Suitability of resin for metal preconcentration

The ability of the resin to preconcentrate metal ions was tested. Volumes of 10 ml of solutions with metal ion concentrations of 10^{-4}–10^{-7} M at the desired pH value were passed through the resin column at a flow-rate of 1.0 ml min^{-1}. Borosilicate glass columns were used. The resin column was 10 × 0.63 cm I.D. Recovery of the metal ion was achieved by treating the resin with 5 ml of a suitable stripping agent. After elution, the resin was rinsed twice with 2 ml of high-purity water; both washings were collected in a 10-ml calibrated flask and then made up to volume. The metal ion concentrations were determined spectrophotometrically.

RESULTS AND DISCUSSION

Sorption of metal ions by batch operation

The sorption of metal ions on N-(hydroxymethyl)thioamide resin at higher concentrations of mineral acid was studied, as that of noble metal ions was previously found to be nearly independent of pH in a higher pH medium [9]. The results (Table I) indicate that the distribution coefficients of the auric ion were larger than 10^5 even with 5 *M* perchloric acid solution. Those of silver, mercury and platinum were somewhat lower, while those of the other metal ions such as Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II), showed almost no adsorption on this resin. For further studies, hydrochloric acid was used instead of perchloric acid; the distribution coefficients obtained (Table I) showed a larger decrease for silver, mercury and platinum, whereas those of gold did not decrease so much and were still large at 3 *M* hydrochloric acid, but obviously decreased at higher concentrations of hydrochloric acid. These results indicate that the synthesized resin was highly selective for noble metal ions in strongly acidic solution, and the competition of the chloride ion with the functional group of the resin increased as the acid concentration increased. These results also suggest that hydrochloric acid could be used as an eluent for the separation of noble metal ions from other transition metal ions.

TABLE I

DISTRIBUTION COEFFICIENTS OF SOME METAL IONS ON N-(HYDROXYMETHYL)THIOAMIDE RESIN AT DIFFERENT CONCENTRATIONS OF MINERAL ACID SOLUTION

Amount of resin: 0.3 g. Amount of each metal ion: 0.01 mmol. Volume of solution: 25 ml.

Metal ion	Acid	Acid concentration (*M*)			
		0.1	2	4	5
Ag(I)	$HClO_4$	317	229	145	51
	HCl	–	6	3	0
Au(III)	$HClO_4$	$>10^5$	$>10^5$	$>10^5$	$>10^5$
	HCl	$>10^5$	$>10^5$	79	25
Cd(II)	$HClO_4$	9	5	<3	<3
	HCl	<1	<0.5	<0.5	<0.5
Co(II)	$HClO_4$	4	<3	<0.5	<0.5
	HCl	<1	<1	<0.5	<0.5
Cu(II)	$HClO_4$	4	<2	<0.5	<0.5
	HCl	<2	<0.5	<0.5	<0.5
Fe(III)	$HClO_4$	<0.5	<0.5	<0.5	<0.5
	HCl	<1	<0.5	<0.5	<0.5
Hg(II)	$HClO_4$	$>10^3$	$>10^3$	$>10^2$	$>10^2$
	HCl	148	26	16	12
Ni(II)	$HClO_4$	<3	<0.5	<0.5	<0.5
	HCl	<1	<0.5	<0.5	<0.5
Pb(II)	$HClO_4$	<1	<0.5	<0.5	<0.5
	HCl	<1	<0.5	<0.5	<0.5
Pt(II)	$HClO_4$	533	103	103	–
	HCl	153	73	32	–
Zn(II)	$HClO_4$	<1	<0.5	<0.5	<0.5
	HCl	<0.5	<0.5	<0.5	<0.5

TABLE II

EFFECT OF FOREIGN LIGANDS ON THE RETENTION OF METAL IONS ON N-(HYDROXYMETHYL)THIOAMIDE RESIN[a]

Volume of solution: 25 ml. Amount of resin: 0.3 g. Amount of metal ion: 0.01 mmol.

Ligand	Retention (%)								
	Cu(II)	Fe(III)	Co(II)	Ni(II)	Zn(II)	Pb(II)	Cd(II)	Hg(II)	Ag(I)
Tartaric acid[b]	1.5	4.5	2.4	~0	~0	5.7	8.4	6.4	45.0
Glycine[c]	91.2	70.3	90.0	100	92.4	100	85.7	73.8	53.1
Glycine[d]	94.4	72.4	91.0	100	95.0	100	88.4	79.3	56.3
EDTA[c]	0.6	~0	2.5	~0	23.5	5.8	7.4	~0	45.6
EDTA[d]	69.3	32.2	76.5	73.2	80.1	73.8	67.2	66.4	54.4
Thiourea[c]	60.3	57.6	77.5	41.9	84.0	97.8	90.4	54.4	14.4
Thiourea[d]	92.8	64.4	87.1	92.1	91.0	97.8	92.4	59.2	20.0
Citrate[c]	99.0	18.6	97.0	92.7	75.4	89.6	97.0	55.4	46.2
Citrate[d]	99.0	53.3	100	100	84.2	97.8	98.0	61.9	46.9

[a] Means of triplicate determinations.
[b] $[L] = 0.1\ M$.
[c] $[L] = 10^{-3}\ M$.
[d] $[L] = 10^{-4}\ M$.

Table II shows the effect of foreign ligands on the retention of metal ions on N-(hydroxymethyl)thioamide resin. The ligands chosen were those most probably competitive with the functional group of the resin. In the presence of 0.1 *M* tartaric acid and 10^{-3} *M* EDTA, most of the metal ions were hardly adsorbed by the resin. Therefore, tartaric acid or EDTA might be the best eluent for the separation of these metal ions. Thiourea was chosen as representative of a sulphur ligand. The results also showed that the sorption increased considerably when the concentration of these ligands was decreased to 10^{-4} *M*. As EDTA might be a very strong ligand in natural water and 10^{-7} *M* EDTA might be a reasonable upper limit to the possible ligand concentration in nature, it can be concluded that the synthesized resin would be very useful in natural water analysis.

Analytical applications

As the synthesized resin showed fast kinetics and selective, strong binding of noble metal ions, the application of this resin in the chromatographic separation of noble metals from base metals or noble metal ion mixtures should be promising.

Separation of metal ion mixture

The resin column has been used for the separation of aqueous metal ion mixtures of Cu–Ag, Cu–Au, Hg–Fe–Cu, Au–Co–Cu–Zn and Au–Hg–Pt–Fe–Cu. Through the use of step gradients with 0.0036–0.036 *M* sulphuric acid, the noble metal ion could be separated from base metal ions with a resolution ranging from 0.75 to 2.5, and with 0.1–1 *M* hydrochloric acid, the noble metal ions could be separated from each other with a resolution ranging from 0.6 to 1.5.

TABLE III

RECOVERY OF CADMIUM(II), COPPER(II) AND LEAD(II) WITH N-(HYDROXYMETHYL)-THIOAMIDE RESIN COLUMN

Resin column: 10 cm × 0.63 cm I.D. Volume of solution: 10 ml. Conditions: 0.1 *M*, pH 5 (acetic acid–sodium acetate buffer). Flow-rate: 1.0 ml $\min^{-1}$. Eluent for Cu(II): 0.1 *M* HNO_3. Eluent for Pb(II) and Cd(II): 0.1 *M* tartaric acid. No. of measurements for each sample: 3.

Metal ion	Metal ion added (μg)	Metal ion found (μg)	Recovery (%)
Cu(II)	0.128	0.128 ± 0.003	100 ± 3
Cd(II)	1.31	1.24 ± 0.03	95 ± 2
Pb(II)	2.07	1.99 ± 0.04	86 ± 2

TABLE IV

RECOVERY OF METAL ION MIXTURES WITH N-(HYDROXYMETHYL)THIOAMIDE RESIN COLUMN

Resin column: 10 cm × 0.63 cm I.D. Volume of solution: 10 ml for Ag–Cu and 500 ml for Ag–Cu–Fe. Flow-rate: 1.0 ml $\min^{-1}$. Eluent for copper(II) or copper(II) and iron(III): 0.2 *M* $HClO_4$. Eluent for gold(III): 12 *M* HCl. Eluent for silver(I): 6 *M* HCl. No. of measurements for each sample: 3.

Metal ion mixture	Metal ion	Metal ion added (μg)	Metal ion found (μg)	Recovery (%)
Au–Cu	Au	39.4	39.0 ± 0.8	99 ± 2
	Cu	63.5	63.5 ± 0.1	100 ± 0
Ag–Cu–Fe	Ag	13.6	10.1 ± 0.5	74 ± 4
	Cu	1.59×10^3	$(1.69 \pm 0.04) \times 10^3$	106 ± 3
	Fe	43.8	43.0 ± 0.9	98 ± 2

Suitability of resin for metal preconcentration

A preliminary investigation was made of the recovery of Ag(I), Au(III), Cu(II), Cd(II), Fe(III) and Pb(II) from dilute solutions at pH 5 and a flow-rate of 1.0 ml $\min^{-1}$. Some metal ions are strongly retained by this resin, and the release procedure involves elution with a strong acid. Table III shows the recoveries of single elements with this resin column. Copper ion was eluted with 0.1 *M* nitric acid, while lead and cadmium ions were eluted with tartaric acid.

Table IV shows the recoveries of metal ion mixtures with the resin column. Mixtures of Au–Cu and Ag–Cu–Fe were tested. Samples of 10 ml of Au–Cu solution showed a satisfactory recovery for both elements. This result indicates the potential of the proposed method for the recovery of gold from Cu–Au mixtures. The anomalously low recoveries obtained for silver ion from Ag–Cu–Fe mixtures could be attributed to the presence of some reduced form of silver ion in the resin column.

ACKNOWLEDGEMENT

The financial support of this study by the National Science Council of the Republic of China is gratefully acknowledged.

REFERENCES

1 J. Weiss, *Fresenius' Z. Anal. Chem.*, 327 (1987) 451.
2 B. Willeford and H. Veening, *J. Chromatogr.*, 251 (1982) 61.
3 J. O'Laughlin, *J. Liq. Chromatogr.*, 7 (1984) 127.
4 G. Nickless, *J. Chromatogr.*, 313 (1985) 129.
5 B. Steinbrech, *J. Liq. Chromatogr.*, 10 (1987) 1.
6 A. R. Timberbaev, O. M. Petrukhin and Y. A. Zolotov, *Fresenius' Z. Anal. Chem.*, 327 (1987) 87.
7 M. V. Main and J. S. Fritz, *Anal. Chim. Acta*, 229 (1990) 101.
8 C. Y. Liu, *J. Chin. Chem. Soc.*, 36 (1989) 389.
9 C. Y. Liu, H. T. Chang and C. C. Hu, *Inorg. Chim. Acta*, 172 (1990) 151.